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FREEZING PARAMETERS AND COMPRESSIONS OF TWENTY-ONE SUBSTANCES TO 50,000 kg/cm².

By P. W. BRIDGMAN

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(Continued from page three of cover)

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INTRODUCTION

In a preceding paper¹ the technique has been developed for measuring the compression of the more compressible substances up to 50,000 kg/cm² and applied to some 46 solid materials. In this paper the method is extended to 21 substances which are liquid under normal conditions; all of these 21 substances are organic except water. The object of this investigation is two-fold. It is in the first place to determine the melting parameters over a wider range than that previously explored,² which, except in the case of water, was 12,000 kg/cm². Apart from the intrinsic interest of obtaining numerical values in the wider range, there is at present some little theoretical interest in making such an extension, because recently the question has been brought up again of the ultimate course of the melting curve and the possibility of a critical point be-

tween liquid and solid.³ In the second place it was desired to obtain as extensive measurements as possible of the p-v-t relations of both liquid and solid phase of the same substance. In spite of the great number of previous determinations of the p-v-t relations of solids and liquids, almost nothing has been done on both liquid and solid phases of the same substance, so that little is known of the change in thermodynamic properties produced by freezing.

METHOD

The technique of the previous work had to be modified to permit in the first place the handling of liquids instead of solids, and in the second place the use of a wider temperature range.

It was hopeless, within the limitations imposed by the magnitude of the pressure range and the small size of the apparatus, to attempt to pack the piston of the pressure vessel against leak by a liquid directly in contact with it. The liquid was accordingly sealed into a collapsible capsule of lead. After much trial the form of the capsule shown in Figure 1 was adopted. This is originally made in two pieces A and B, which are then fused together. Various attempts at soldering were without success. Fusing together

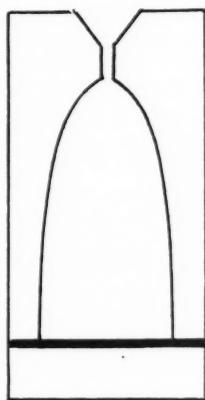


FIG. 1. The lead capsule for containing the liquids. The opening at the top is sealed by a lead plug fused with a condenser discharge.

is accomplished in an atmosphere of hydrogen. The bottom disc B is melted in a cup shaped mold in a miniature electric furnace. The part A is mounted in a holder by which it may be rotated about its vertical axis, and which may also be displaced vertically. When B is melted A is brought down until its lower edge dips into the molten metal, and it is then spun about its vertical axis until it is completely wet by the liquid metal and good contact made, as shown by the liquid lead climbing up the side of A. All this takes place in a stream of dry hydrogen. Filling is accomplished through the fine hole in the top by immersing the capsule under the liquid and applying and removing a vacuum several times and finally boiling the liquid. The seal is made electrically. A pointed lead wire is driven by a light hammer blow into the depression at the top of A. The wire and A are attached to the two coatings of a previously charged condenser so that a discharge takes place, fusing the lead locally, just before mechanical contact occurs. The soundness of the seal is tested by placing the sealed capsule under water in a test tube, which is heated sufficiently above the boiling point of the liquid to visibly distend the capsule. After the test the capsule is restored to shape by squeezing in the wire chuck of a lathe. The quantities of lead and liquid were determined by weighing, both before inserting in the pressure apparatus and after the run, as a check. The quantity of liquid was of the order of 0.2 or 0.3 gram, and the checks indicated an accuracy of 0.001 gram or better. In addition to weight of lead and liquid, the weights were also always recorded of the various steel packing cones and rings and the carboly closure block and a wrapping of copper foil. The latter was always interposed as a precaution, perhaps unnecessarily, against rupture of the steel containing vessel by alloying between lead and steel at these high pressures. The weights of all the contents of the pressure vessel obviously affect the total compression and corrections were calculated for slight variations in the amount of steel etc. from run to run; these corrections were usually negligible.

At 50,000 kg/cm² the volume of the liquids of this paper is on the average about 0.6 of the initial volume; it is evident therefore that the walls of the capsule are subject to and must withstand heavy distortions. The distortion is so great that only a few applications of pressure to the capsule are possible. After considerable

experience the routine was adopted of not attempting more than two applications of pressure, after which the apparatus was taken down and set up again with a new filling. The usual form of the distortion of the capsule is a thickening of the top, and thinning and eventual necking down and leak at the bottom part. The precise manner of deformation is sensitive to slight changes in the shape of the capsule; a comparatively slight change from the shape indicated in Figure 1 results in necking down near the top instead of at the bottom. The precise manner of distortion is also determined by the absolute compression of the contents of the capsule.

The use of lead as the material of the capsule, instead of the more easily deformable indium which was used in the previous work, was necessitated by the fact that the temperature range contemplated was above the melting temperature of indium. In the former work measurements were made at room temperature and $-80^{\circ}\text{C}.$; in this work the temperature ranges upward from room temperature usually to 175° but on one occasion to 225° . No measurements were attempted below room temperature; for one thing the greater stiffness of the lead would have introduced error. Temperature control was by an electrically heated, regulated, and stirred oil bath, in the same container that was used for the dry ice in the previous work. At temperatures above 100° the steel pressure vessels are materially weakened; at least one particular kind of rupture is much more frequent, namely across the threads at the closure end. I had originally been troubled by this same sort of rupture at room temperature on first beginning work with the apparatus for 50,000, and avoided it by changing the external angle of the containers. No further change in this direction is now feasible, however, and after attempting a number of different devices I have come to accept this as a necessary limitation of the present design. The result is that in the following compressions above 100° are given to a maximum pressure of only 45,000 instead of 50,000. Even with this reduction, ruptures at the higher temperatures have been discouragingly frequent, and account for the fact that a number of compressions in the following are not given over the full temperature range.

The method is, as before, differential. Piston displacement is measured as a function of pressure when the vessel is filled with capsule and liquid, and then a comparison run is made with the capsule replaced by a known amount of

steel and an equal amount of lead. The difference of displacement of the two runs is taken.

The distortion of the vessel approximately cancels from this difference, leaving the difference of compression of steel and liquid. In the following my new results for the compression of steel up to 30,000 were used,⁴ extrapolating from 30,000 to 50,000, which should make no appreciable error in view of the small compressibility of steel compared with that of the various liquids. The compression of lead also enters the results as a small correction, because it was usually not possible to use exactly the same amount of lead in the two runs. The values for the compression of lead used in this correction were obtained from unpublished results also up to 30,000, and extrapolated by Murnaghan's formula⁵ to 50,000. The values assumed for $\Delta V/V_0$ of lead were: at 25° 0.051 and 0.091 at 25,000 and 50,000 respectively; at 75° 0.052 and 0.092 at the same pressures, and at 125° and 175° the values given by linear extrapolation from 25° and 75°.

The calculations were made by the same formulas as in the preceding work.

The melting parameters and the compressions were determined in two independent sets of experiments. The necessity for this arose from the fact that measurements of compression demand operation on a definite time schedule in order that the distortions connected with hysteresis and similar effects may be reproducible, whereas the freezing measurements cannot be conducted on a fixed time schedule because the lag in the appearance of the solid phase and the velocity of crystallization to the solid after its nucleus has been formed vary greatly from substance to substance. It is fortunate in view of this that hysteresis produces no essential error in the determination of the freezing parameters.

As in all my earlier work, the freezing parameters which were measured were equilibrium pressure and temperature and the corresponding change of volume. At each temperature two values of the change of volume were obtained, with increasing and decreasing pressure; the average of these was usually taken. The latent heats etc. are then calculated by an application of Clapeyron's equation. All the determinations were made by isothermal variation of pressure; the method of variation of temperature at constant volume which has been used in some of my work was not well adapted to the apparatus and was not used. In general the melting parameters were determined at 25° intervals. Pressure was

not varied over the entire range, but by only so much on each side of the equilibrium pressure that the reactions had surely run to completion and the full width of the frictional hysteresis loop due to reversal of direction of change of pressure attained. Pressure was varied in steps of 400 kg/cm² instead of the steps of 2,000 used in measuring compressions. The regular time schedule was used when the reaction from one phase to the other was not running; when the reaction was running, however, it was customary to wait after each change of pressure until the reaction had approximately ceased. The melting pressure on any isotherm was taken from the readings with decreasing pressure, since the solid phase does not superheat, whereas the liquid phase almost always subcools. The equilibrium pressure was taken as the mean of the last pressure before melting starts and the first pressure after melting just begins, as shown by the change of volume, corrected by one half the width of the frictional hysteresis loop above and below the melting. Since the pressure steps are 400 kg/cm², the error in a single melting pressure thus determined should not be more than 200 kg/cm².

Subcooling of the liquid becomes an increasingly prominent phenomenon at high pressures; the reluctance of the solid phase to appear constituted one of the major experimental difficulties of this work. In several cases the melting curves could not be carried to as high temperatures as it might appear they should, because pressures higher than 50,000 would have been required to induce the appearance of the solid phase. A phenomenon found by Tammann imposed a restriction on the manipulation, namely the ease of formation of a nucleus of the solid out of the liquid passes through a maximum with increasing pressure. This means that the solid cannot be induced to appear merely by raising pressure to the maximum beyond the equilibrium pressure and waiting, but if the solid will not appear within a practical time on increasing pressure to the most favorable value, there is nothing to be done. As a consequence of these various lag phenomena it was possible for one substance, ethyl acetate, to run two sets of compression curves, one for the metastable liquid in the domain of the solid up to the maximum pressure, and the other for the solid. For another substance, methyl cyclohexane, it was possible to get through the region of appreciable reaction velocity with sufficient speed to carry a large fraction of the material up to the maximum

pressure in the form of the subcooled liquid and obtain measurements of its compression.

Compressions were measured at 50° intervals. It was the original intention to measure all compressions at 25° (room temperature), 75°, 125°, and 175°, but in view of the experimental difficulties already described, the two higher temperatures were dispensed with in six cases. All the compressions given in the following are the means obtained with two or more independent set-ups in different pressure vessels. In general, one set-up was used twice, at 25° and 75° or at 125° and 175°. The pressure vessels were calibrated by blank runs with iron at all four temperatures; the cases were distressingly numerous in which the vessel survived only the calibrating runs. Twenty four pressure vessels were used in the measurements of compression. Of these, four only were used for the measurements at 25° and 75° to a pressure maximum of 50,000, with an average life of 24.5 exposures to the maximum. Twenty vessels were used for the measurements at 125° and 175° to a maximum of 45,000, with an average life of 5.0 exposures.

The compressibility of liquids drops off very fast in the first few thousand atmospheres; the curves of piston displacement against pressure are initially very steep, rapidly flattening out. Error from friction is especially large at the lower end of the pressure range, where the curve is steep and the forces relatively small. As a consequence, I did not attempt to use the readings to give any results at pressures lower than 5,000, and the volume decrements given in the following are all calculated from 5,000 as the zero. For the compressions up to 5,000 it is necessary to rely on other work. For a number of the following substances these previous measurements have been made, but unfortunately there are a number which have not been previously measured, and for them the conversion of the present measurements into absolute volumes as a function of pressure must wait for future measurements. Not only are the values below 5,000 obtained by the present method too inaccurate, but something of the same inaccuracy also affects the measurements between 5,000 and 10,000. I have given the preference to the former values in the following, and have corrected the values of the present work at pressures higher than 10,000 by an additive term so chosen as to reduce the present results to agreement with the former ones in the interval 5,000 to 10,000. The magnitude of the correction so applied is given for the various

substances in the following detailed description. In no case are there previous measurements between 5,000 and 10,000 at the two higher temperatures, 125° and 175°. At pressures above 5,000 the behavior of liquids is settling down to linearity with temperature, so that in a number of instances it seemed best to extrapolate the previous values for 25° and 75° up to 125° and 175° for the interval 5,000 to 10,000, and apply the additive correction so determined to the present measurements at 125° and 175°. The details are given in the following.

The accuracy of the results probably does not in general, although there may be a few exceptions, justify the retention of more than three significant figures, and this is all that are given in the following final results. All the results were calculated to four figures, however, and the averages of the two runs were subjected to a smoothing by graphical methods to give smooth first differences out to the fourth decimal place. The results given in the following were obtained by contraction of these four figure results. Any apparent lack of smoothness in the first differences arises from the play of the fourth figure. As a rough indication of the accuracy, the deviations of the individual runs from the mean at the maximum pressure are given, usually to the fourth figure. This deviation does not always tell the complete story, however, because the maximum percentage deviations are not always at the maximum pressure. It must also be considered that with so many substances there must be some for which the error in the final result is greater than indicated by the agreement between the individual measurements, and some for which the error is less than would be inferred from the divergence of the two measurements.

An additional indication of the accuracy is given by the smoothness of the figures across the columns of the tables, that is, by the smoothness with respect to temperature at constant pressure. In adjusting the results, smoothings were made with respect to pressure at the various constant temperatures. The only cross smoothings were occasionally at the lowest pressure, as already described. At the upper pressures of the range the different isotherms are therefore essentially independent, and the smoothness of the progression from column to column affords a check on the probable accuracy.

Not only were the compressions adjusted as described to agree with my previous values at the lower end of the pressure range, but they were

also adjusted, for those substances which freeze, to be consistent with the values here found for the melting parameters, in particular for the change of volume. The experimental values for the change of volume on freezing always show some scatter; the values obtained during the compression measurements were not obtained by a procedure particularly well adapted to give good values for this particular parameter, and there is no question but that the values obtained with the other set-ups when the manipulation was particularly made to give the freezing parameters should be preferred. The adjustments thus demanded were not large, and it was not possible to devise any unique procedure for making them, but the procedure was varied according to the details of the behavior of the different substances. The uncertainty would be expected to be greatest in general in the volumes of the solid just beyond the freezing point, since freezing might not have been completed here because of subcooling or perhaps the effect of impurity. The rough general procedure was to retain without adjustment the values given directly by the readings for the liquid up to the freezing pressure, then at the freezing pressure to give the solid the volume demanded by the special determinations of the melting parameters, and then to distribute the alterations thus demanded in the measured compressions of the solid above the freezing pressure over the entire pressure range, tapering off linearly to zero adjustment at the top pressure. The numerical details are given in the following.

DETAILED PRESENTATION OF DATA

Methyl Alcohol. The material was specially purified by redistillation by Mr. L. D. Berger in the Chemical Laboratory of Harvard University. Compressions were measured at all four temperatures in four different pressure vessels; at the lower two temperatures with two independent set-ups, and at the two higher temperatures with three set-ups. At 25° the material froze on one of the two runs, and rough values of the freezing parameters at this temperature were obtained. However, the freezing was very sluggish, and on the other set-up the material was carried in the metastable liquid condition to the maximum pressure. As a consequence values were obtained at 25° for the compressions above the melting point of both liquid and solid phases. In view of the sluggishness of the freezing and the magnitude of the freezing pressure at 25°, 30,000, the special effort was not made that would have been

necessary to obtain other points on the freezing curve at higher temperatures.

In order to bring the volume decrements between 5,000 and 10,000 into agreement with the previous values a subtractive correction of 0.0009 was applied to all readings at 25° and of 0.0020 to the readings at 75°. Subtractive corrections of 0.002 at 125° and 0.005 at 175° were applied to give a smoothly extrapolated isobar at 10,000, but these two corrections are obviously in some doubt. At 25° the compressions of the two runs before adjustment differed at the maximum pressure by 4.6% from the mean and at 75° by 8.6%. At 125° the extreme deviation from the mean at the maximum pressure was 4.2% and at 175° 3.8%. These deviations are somewhat larger than the average. There was no particular consistency in the deviation from the mean given by any one pressure vessel.

TABLE I
METHYL ALCOHOL

ΔV , in cm^3 per 0.792 gm. from 5,000 kg/cm^2 as zero

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.819)	.000 (.838)	.000 (.859)	.000 (.881)
10,000	.062	.066	.073	.082
15,000	.099	.106	.117	.128
20,000	.125	.135	.149	.161
25,000	.145	.157	.174	.187
30,000	.161 .179*	.173	.194	.208
35,000	.173 .189	.187	.210	.226
40,000	.183 .198	.198	.223	.240
45,000	.191 .206	.208	.234	.253
50,000	.199 .215	.218		

* Solid phase in this column.

The compressions are shown in Table I; in the 25° column the compressions of both liquid and solid are given above the freezing point. The figures in parentheses in the 5,000 row are the total volumes at 5,000 as given by previous work.⁶ By subtracting the tabulated volume decrements the volume itself may be obtained as a function of pressure and temperature. The plan was adopted of tabulating consistently the volume decrements instead of the volume because for a number of substances only the decrements are known.

Ethyl Alcohol. The material I owe to Professor F. G. Keyes of M. I. T. who had especially purified it for use as one of his standard liquids to give one of the temperature fixed points of low temperature thermometry by its freezing point. Obviously the purity has to be high for such a

TABLE II
ETHYL ALCOHOL
Freezing Parameters

Pressure kg/cm ²	Temp. °C	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm ^o
0	-117°.3						
5,000	- 76.						
10,000	- 39.						
15,000	- 5.	.0064	.0443	1,850	660	1,190	6.93
20,000	+ 25.	.0059	.0435	2,200	870	1,330	7.38
25,000	54.	.0056	.0428	2,480	1,070	1,410	7.58
30,000	82.	.0055	.0420	2,700	1,260	1,440	7.60
35,000	109.	.0054	.0412	2,910	1,440	1,470	7.66

use. Compressions were measured at all four temperatures, with two independent set-ups at the two lower and three at the two upper temperatures, in four different pressure vessels. In addition, the freezing parameters were determined at four temperatures in two vessels; the maximum freezing temperature attempted was 100°, where the equilibrium pressure is 33,200 kg/cm². The increasing sluggishness of the reaction did not permit the determination of freezing parameters at higher temperatures.

In order to secure agreement with the previous measurements⁷ an additive correction of 0.0050 was applied at 25° and of 0.0003 at 75°. The corresponding corrections, obtained by extrapolation, were 0.003 at 125° and 0.003 at 175°. In order to secure agreement with the independently measured freezing parameters further adjustments were made as explained; these were at the maximum 0.0020 at 25° and 0.0010 at 75°. The deviation from the mean at the maximum pressure of the compressions of the two independent

runs was 0.3% at 25°, 1.8% at 75°, and the extreme deviation at the two higher temperatures from the means was 3.7% at 125° and 4.1% at 175°.

The freezing parameters are given in Table II and Figure 2, and the compressions in Table III. Notice that the freezing parameters are given in terms of one gram of material and the compressions in terms of that amount of material which occupies one cubic centimeter at room temperature. This is the usual usage; following this usage means that one cannot pass directly from the volume discontinuities listed under the freezing parameters to the difference of compressions for liquid and solid listed in the tables of compressions, but one must multiply by the density. Notice also that the latent heats etc. are given in mechanical units instead of in calories as is often done; the mechanical units are given directly by Clapeyron's equation, and appear to be the most natural to use under the circumstances.

n-Propyl Alcohol. The material was purified by distillation by Mr. L. D. Berger, who reported the values: B. P. 96°.31 C at 760.3 mm. $n_D^{17.8}$ 1.3860. Compressions were measured at all four temperatures, with two independent set-ups at 25° and 75° and with three at 125° and 175° in five pressure vessels. The material did not freeze under pressure in the temperature range.

To secure agreement with previous results⁸ in the pressure range 5,000 to 10,000 a subtractive correction of 0.0043 was applied to the results at 25° and of 0.0072 at 75°. No correction was applied at 125° or 175°, although an argument could be made for an additive correction of 0.002 at 175°. The divergence from the mean of the two independent runs at the maximum pressure was 1.1% at 25°, and 0.3% at 75°. The corresponding extreme deviations were 0.4% at 125° and 2.8% at 175°.

The compressions are given in Table IV.

TABLE III
ETHYL ALCOHOL

ΔV , in cm³ per 0.789 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000 (.819)	.000 (.836)	.000	.000
10,000	.063	.069	.071	.076
15,000	.100	.109	.113	.119
20,000	.128	.137	.144	.151
25,000	.163*	.159	.168	.175
28,700	.181	.174		
		.207*		
30,000	.196	.211	.187	.195
35,000	.209	.223	.203	.211
40,000	.220	.233	.217	.225
45,000	.230	.242	.230	.238
50,000	.238	.250		

* Solid below this.

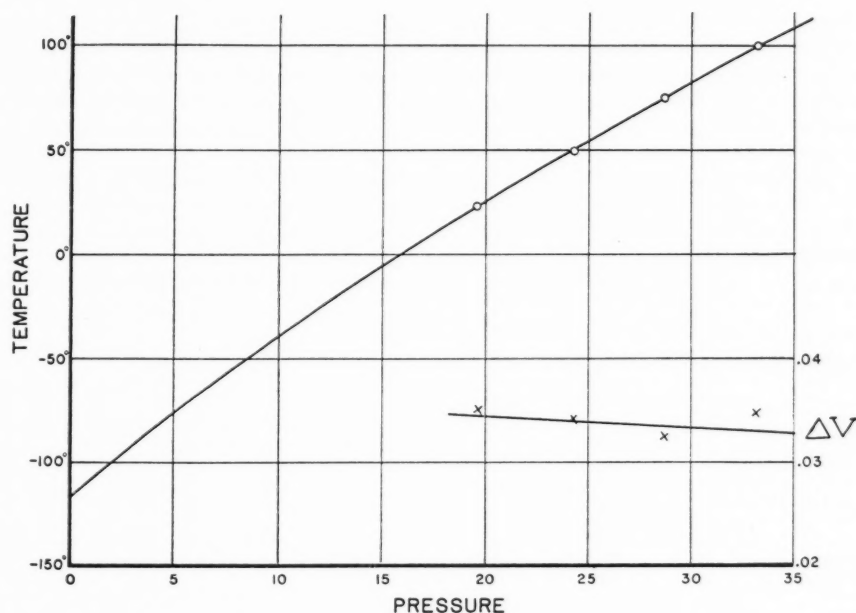


FIG. 2. The freezing parameters of ethyl alcohol. The freezing temperatures as a function of pressure are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

TABLE IV
n-PROPYL ALCOHOL

ΔV , in cm^3 per 0.804 gm, from 5,000 kg/cm^2 as zero.

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.840)	.000 (.857)	.000	.000
10,000	.054	.058	.064	.068
15,000	.088	.096	.106	.114
20,000	.113	.122	.135	.144
25,000	.134	.143	.157	.168
30,000	.151	.160	.176	.187
35,000	.166	.174	.192	.203
40,000	.179	.187	.207	.217
45,000	.191	.199	.219	.229
50,000	.201	.210		

TABLE V
i-PROPYL ALCOHOL

ΔV , in cm^3 per 0.786 gm, from 5,000 kg/cm^2 as zero.

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.833)	.000 (.850)	.000	.000
10,000	.060	.065	.070	.075
15,000	.096	.104	.110	.120
20,000	.121	.131	.139	.150
25,000	.141	.152	.161	.174
30,000	.158	.170	.179	.193
35,000	.173	.185	.194	.208
40,000	.186	.197	.206	.220
45,000	.197	.208	.217	.231
50,000	.207	.217		

i-Propyl Alcohol. The material was obtained from Prof. Brunel many years ago. On redistillation it all boiled at $82^\circ.7$ except the very last at $82^\circ.8$. This material did not freeze in the temperature range of this work, so only the compressions were measured, at all four temperatures, with two independent set-ups at each temperature, and in four different pressure vessels.

The additive corrections were 0.0011, - 0.0014, 0.0017, and - 0.0021 at 25° , 75° , 125° , and 175°

respectively. At 25° the deviations from the mean compression at the maximum pressure were 1.0%, at 75° 0.9%, at 125° 0.5%, and at 175° 1.2%.

The compressions are given in Table V. The material has been previously measured.⁹

n-Butyl Alcohol. The material was specially purified by distillation by Mr. L. D. Berger. Compressions were measured at all four temperatures: with two different set-ups and in two different pressure vessels at 25° and 75° , and

with three set-ups and in three vessels at 125° and 175°. The freezing parameters were determined at 25° intervals from 25° to 150° in two different vessels with two different set-ups.

Because of the low freezing pressure, previous values¹⁰ for the compression exist only at 75°. Here a subtractive correction of 0.0024 was applied. No attempt was made to estimate a probable correction at 25°, the value given by the unadjusted measurements appearing plausible enough. At 125° and 175° the additive cor-

rections were .0009 and - .0017. At 25° the deviation of the two runs from the mean at the maximum pressure was 4.5%, at 75° 3.2%, at 125° 0.5%, and at 175° 0.8%. In order to secure agreement with the directly determined freezing parameters a further adjustment rising at its maximum to 0.0014 had to be applied at 75°; no such adjustment was necessary at 25°. The adjustment at 125° was .0009.

The freezing parameters are given in Table VI and Figure 3, and the compressions in Table VII.

TABLE VI
n-BUTYL ALCOHOL
Freezing Parameters.

Pressure kg/cm ²	Temp. °C.	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
0	- 89°.8						
5,000	- 33.						
10,000	+ 12.	.0080	.0478	1,690	480	1,210	5.97
15,000	49.	.0068	.0432	2,050	650	1,400	6.35
20,000	80	.0058	.0399	2,430	800	1,630	6.88
25,000	108	.0052	.0373	2,730	930	1,800	7.17
30,000	132	.0047	.0352	3,040	1,070	1,970	7.49
35,000	155	.0042	.0333	3,390	1,170	2,220	7.92

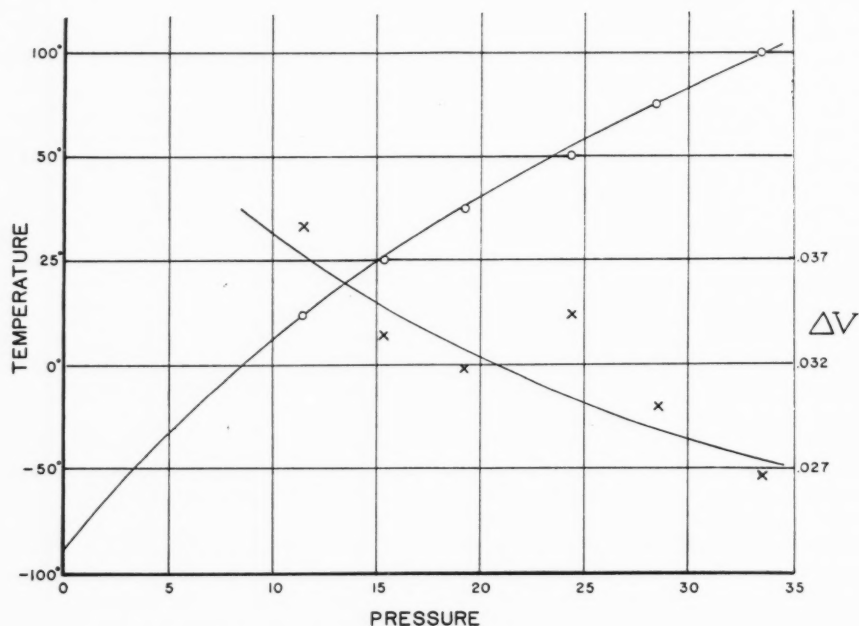


FIG. 3. The freezing parameters of n-butyl alcohol. The freezing temperatures as a function of pressure are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

TABLE VII

n-BUTYL ALCOHOL

 ΔV , in cm^3 per 0.810 gm, from 5,000 kg/cm^2 as zero

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.845)	.000 (.862)	.000	.000
10,000	.058	.063	.068	.074
11,700	.072			
	.109*			
15,000	.125	.100	.110	.119
19,000		.122		
		.155*		
20,000	.144	.159	.140	.150
25,000	.160	.178	.165	.174
27,000			.174	
			.203*	
30,000	.173	.192	.212	.194
35,000	.185	.204	.225	.210
40,000	.195	.214	.236	.224
45,000	.205	.223	.244	.235
50,000	.213	.231		

* Solid at higher pressures.

TABLE VIII

n-AMYL ALCOHOL

 ΔV , cm^3 per 0.817 gm, from 5,000 kg/cm^2 as zero

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.843)	.000 (.860)	.000	.000
10,000	.056	.061	.067	.073
15,000	.093	.100	.107	.115
20,000	.119	.127	.136	.146
25,000	.140	.149	.159	.170
30,000	.157	.167	.178	.189
35,000	.172	.183	.194	.205
40,000	.184	.196	.207	.219
45,000	.194	.207	.218	.230
50,000	.203	.217		

n-Amyl Alcohol. The material was obtained many years ago from Prof. J. Timmermans of the Bureau Belge d'Étalons Chimiques. Its constants have been described in a previous paper.¹¹ The material did not freeze in the range of this work.

TABLE IX

ETHYL BROMIDE

Freezing Parameters

Pressure kg/cm^2	Temp. °C	Slope $d\tau/dp$	ΔV cm^3/gm	Lat. Ht. $\text{kg cm}/\text{gm}$	$p\Delta V$ $\text{kg cm}/\text{gm}$	ΔE $\text{kg cm}/\text{gm}$	ΔS $\text{kg cm}/\text{gm}^\circ$
0	-119°.						
5,000	- 70.						
10,000	- 29.						
15,000	+ 5	.0062	.0189	845	280	560	3.03
20,000	34	.0053	.0159	916	320	600	2.98
25,000	58	.0045	.0133	975	340	630	2.94
30,000	80	.0039	.0110	996	330	670	2.81

TABLE X

ETHYL BROMIDE

 ΔV , cm^3 per 1.430 gm, from 5,000 kg/cm^2 as zero.

Pressure kg/cm^2	ΔV			
	25°	75°	125°	175°
5,000	.000 (.814)	.000 (.823)	.000	.000
10,000	.061	.066	.071	.076
15,000	.099	.104	.116	.122
18,400	.120			
	.144*			
20,000	.151	.130	.147	.154
25,000	.171	.152	.171	.178
28,500		.167		
		.184*		
30,000	.188	.189	.191	.198
35,000	.201	.203	.206	.213
40,000	.212	.214	.218	.226
45,000	.222	.223	.229	.237
50,000	.230	.231		

* Solid below this.

Compressions were measured at all four temperatures, with two different set-ups at each temperature, and in four different pressure vessels.

The additive corrections imposed by previous work¹² were 0.0024, - 0.0026, 0.0002, and - 0.0019 at 25°, 75°, 125°, and 175° respectively. The deviations of the independent runs from the means at the maximum pressure were 0.1%, 0.06%, 4.3%, and 1.1% at the four temperatures respectively.

The compressions are given in Table VIII.

Ethyl Bromide. The material was specially distilled by Mr. L. D. Berger. The freezing parameters were determined at three temperatures, 25°, 50°, and 75°, with a single set-up. More points on the freezing curve were not attempted because of the very great subcooling; at 75° the equilibrium pressure is 28,000, but it

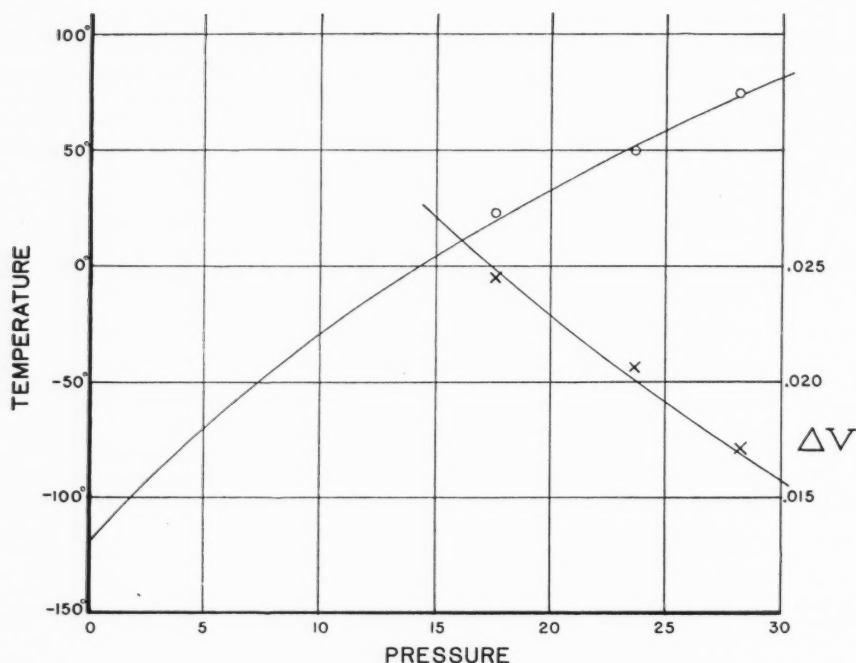


FIG. 4. The freezing parameters of ethyl bromide. The freezing temperatures as a function of pressure are shown by the circles, with the scale to the left, and the *proportional* changes of volume by the crosses, with the scale to the right.

TABLE XI
n-PROPYL BROMIDE
Freezing Parameters

Pressure kg/cm²	Temp. °C	Slope $d\tau/dp$	ΔV cm³/gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
0	-110°						
5,000	- 56						
10,000	- 8						
15,000	+ 34	.0079	.0229	890	340	550	2.90
20,000	71	.0072	.0197	940	390	550	2.74
25,000	105	.0067	.0174	990	440	540	2.61
30,000	138	.0062	.0157	1,040	470	570	2.52
35,000	169	.0059	.0143	1,070	500	570	2.42
40,000	197	.0056	.0131	1,090	520	570	2.32

required the application of 45,000 to induce freezing to begin. Compressions were measured at all four temperatures, with two different set-ups and in two different pressure vessels at 25°, 75° and 175°, and in three different pressure vessels at 125°. The additive corrections necessary to secure agreement with previous work¹³ were 0.0021 at 25°, 0.0026 at 75°, - 0.0028 at 125°, and - 0.0070 at 175°. In order to secure agreement between the compression runs and the

determinations of freezing parameters an additional distributed adjustment rising to the maximum of 0.0043 at 25° and 0.0016 at 75° was applied. The deviations from the mean at the maximum pressure were 2.6% at 25°, 3.2% at 75°, 0.5% at 125°, and 0.7% at 175°.

The freezing parameters are given in Table IX and Figure 4 and the compressions in Table X.

n-Propyl Bromide. The material was redistilled by Mr. L. D. Berger who reported: B. P. 71°.5 at

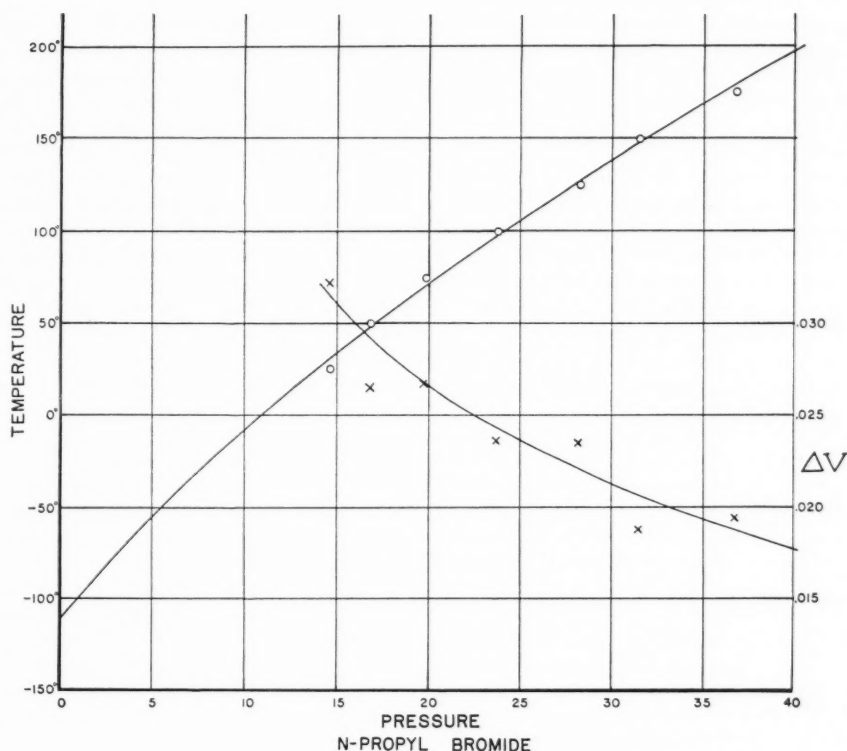


Fig. 5. The freezing parameters of n-propyl bromide. The freezing temperatures as a function of pressure are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

760 mm. n_D^{18} 1.4341. Compressions were measured at the four temperatures, with two different set-ups at each temperature and in four different pressure vessels. The freezing parameters were determined at 25° intervals from 25° to 175° with three different set-ups and in three different pressure vessels.

The additive corrections applied to secure agreement with the previous compressions¹⁴ between 5,000 and 10,000 were 0.0036 at 25° and 0.0007 at 75°. To secure agreement with the independently measured freezing parameters additional corrections of a maximum of 0.0034 at 25°, 0.0006 at 75°, and .0023 at 125° were applied. The deviation from the mean at the maximum pressure was 1.8% at 25°, 1.8% also at 75°, 2.9% at 125°, and 0.0 at 175°.

The freezing parameters are shown in Table XI and Figure 5, and the compressions in Table XII.

TABLE XII

n-PROPYL BROMIDE

 ΔV , cm³ per 1.353 gm. from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000 (.824)	.000 (.843)	.000	.000
10,000	.062	.067	.072	.077
14,000	.093 .125*			
15,000	.131	.106	.114	.119
20,000	.154	.136	.143	.149
20,600		.140		
25,000	.171	.166*	.166	.173
28,000		.182	.178 .200*	
30,000	.184	.196	.207	.193
35,000	.193	.206	.219	.208
40,000	.202	.215	.231	.221
45,000	.209	.222	.241	.234
50,000	.216	.228		

* Solid at higher pressures.

n-Butyl Bromide. The material was prepared by distillation by Mr. L. D. Berger. Compressions were measured at 25° and 75°; it does not freeze in the present range.

An additive correction of 0.0034 was applied at 25° and of 0.0013 at 75° to secure agreement with previous work.¹⁵ The deviations from the means at the maximum pressure were 0.1% at 25° and 1.5% at 75°.

The compressions are given in Table XIII.

TABLE XIII

n-BUTYL BROMIDE

 ΔV , cm³ per 1.275 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25°	75°
5,000	.000 (.826)	.000 (.844)
10,000	.062	.067
15,000	.098	.105
20,000	.125	.133
25,000	.148	.155
30,000	.166	.173
35,000	.182	.189
40,000	.195	.202
45,000	.207	.214
50,000	.218	.224

Ethyl Acetate. The material was from Timmermans.¹¹ Runs were made at all four temperatures; at 25° and 75° with four set-ups and in four different pressure vessels, and at 125° and 175° with three set-ups and in three vessels. The material freezes very sluggishly. If the normal time schedule of pressure increments of 2,000 at two minute intervals is adhered to, freezing does not occur at all with increasing pressure, but the subcooled liquid is carried up to the maximum pressure. On release of pressure, however, freezing occurs on sufficiently close approach to the melting point. This has a paradoxical appearance, for a phase change which runs with decreasing volume is initiated by a decrease of pressure. The paradox consists in the apparent contradiction with the requirement of thermodynamics that the phase stable at the lower pressure have the larger volume. A moment's consideration shows, however, that the paradox is only superficial. The freezing on decreasing pressure occurs so close to the equilibrium point that it is easy to smooth across the bulge thereby produced on the decreasing curve, thus obtaining the normal increasing and decreasing curves for the liquid over the entire range, from which the compression of the liquid up to the maximum pressure can be

obtained in the regular way. On the other hand the solid can be induced to appear if one delays a suitable time in the neighborhood of the freezing point with increasing pressure, and in this way the compressions of the stable phases, liquid below melting pressure and solid above, may be obtained in the regular way. Of the four sets of runs at 25° and 75°, two were so manipulated as to give the liquid over the entire range and the other two so as to give liquid and solid in their regions of stability. At 125° freezing was encountered on two of the three runs, so that these runs give the compression of the solid in the upper part of the range. On the third run at 125° the substance remained liquid over the entire range. No freezing occurred during any of the three runs at 175°.

There are no previous measurements on this material, so the usual additive corrections could not be applied. The low pressure values appear reasonable without correction. The deviations from the mean of the compressions of the subcooled liquid were at the maximum pressure 2.0% and 4.3% at 25° and 75° respectively; the corresponding deviations for the solid were 0.5% and 1.1%.

The compressions of the solid and liquid phases are given in Table XIV. The freezing parameters

TABLE XIV

ETHYL ACETATE

 ΔV , in cm³ per 0.899 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000	.000	.000	.000
10,000	.059	.066	.069	.074
12,100	.076	.107*		
15,000	.095	.122	.111	.118
20,000	.122	.143	.141	.149
23,800		.151	.181*	
25,000	.144	.161	.157	.165
30,000	.160	.176	.174	.184
31,860			.190	.213*
35,000	.174	.188	.189	.211
40,000	.185	.198	.201	.220
45,000	.195	.207	.211	.227
50,000	.203	.215	.220	.234

* Solid in this column.

at 25° and 75° may be taken from this table. These parameters are probably not as accurate as those for other materials determined by manipulations made for the express purpose; in particular the very small drop in the volume contraction

on freezing on passing from 25° to 75° is suspicious.

n-Amyl Ether. The material was obtained many years ago from Timmermans under the name "n-amyl oxide," one of his standard liquids.¹¹ It has been kept sealed in glass in the dark.

Runs were made with two set-ups and two pressure vessels at both 25° and 75°. Freezing occurs at a low pressure, so that most of the compressions are for the solid phase. The freezing parameters were determined only incidentally during the measurement of the compressions, without using small pressure steps or deviating from the regular time schedule. The freezing parameters implicitly contained in the table of compressions are therefore probably not as accurate as usual. In particular, the large drop in the change of volume on freezing on passing from 25° to 75° is suspicious.

There are no previous measurements for comparison at the low pressures. The deviation of

the two runs from the mean at the maximum pressure was 1.4% at 25° and also 1.4% at 75°.

The compressions are shown in Table XV.

Chloroform. The material was from Prof. F. G. Keyes at M. I. T.

Compressions were measured at all four temperatures with two different set-ups at each temperature and in five pressure vessels. The freezing parameters were determined at nine temperatures, at 25° intervals from 25° to 225°, with four different set-ups, all in the same pressure vessel. Freezing is sharp and the manipulations easily made. The measurements were limited by the rapid rise of the melting curve and the attendant high temperatures rather than by the high pressures. On three occasions, at 100°, 175°, and 200°, clean cut anomalous results were obtained, for which the natural explanation is the existence of another form of the solid. It appears that when the liquid is carried beyond its normal melting curve the subcooled liquid may freeze to a new form of the solid, with a volume decrement only about two thirds of that when freezing to the normal form. This new form of the solid appears to be absolutely unstable with respect to the normal form over the entire range of these measurements, for no reversible transitions were found, but after a longer or shorter interval it flops irreversibly to the normal solid with the outstanding remaining one third of the volume decrement. The identity of the solid to which the unstable form flops is established as the normal solid because it exhibits normal melting on release of pressure.

There are no previous measurements for comparison. At 25° the melting pressure is so low that there is much uncertainty as to what the true compression of the liquid is at the freezing pressure, 6,200 kg/cm²; as far as these measurements go, the entire curve at 25° might be raised or lowered by a small constant amount. At 25° the

TABLE XV

n-AMYL ETHER

 ΔV , cm³ per 0.774 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25°	75°
5,000	.000	.000
7,500	.031	
10,000	.078*	
15,000	.094	.063
20,000	.119	.101
25,000	.140	.130*
30,000	.158	.152
35,000	.173	.170
40,000	.186	.184
45,000	.197	.196
50,000	.207	.207
	.217	.217
		.227

* Solid below this.

TABLE XVI

CHLOROFORM

Freezing Parameters

Pressure kg/cm ²	Temp. °C	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
0	- 63°.5	.0154					
5,000	+ 10.	.0140	.0430	870	220	650	3.07
10,000	76.	.0126	.0354	980	350	630	2.81
15,000	137.	.0116	.0301	1,070	450	620	2.59
20,000	192.	.0106	.0262	1,160	520	630	2.47
25,000	243	.0096	.0231	1,240	580	660	2.40

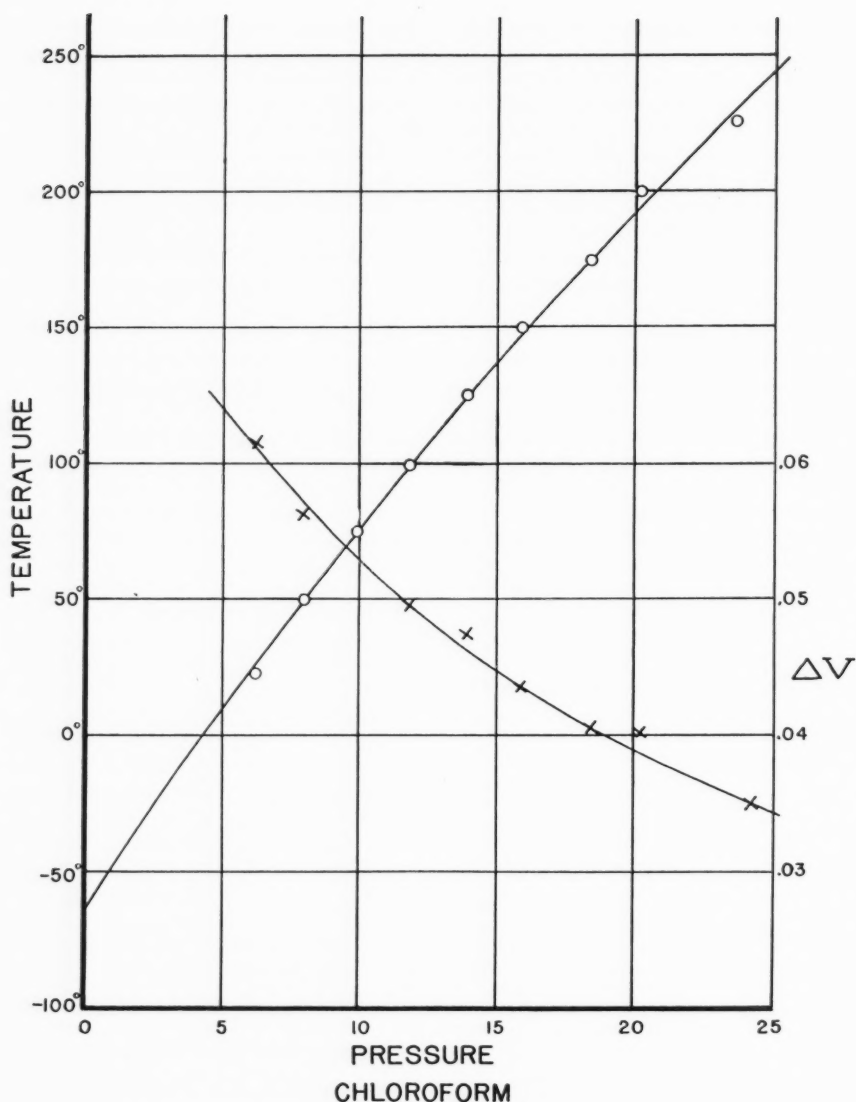


FIG. 6. The freezing parameters of chloroform. The freezing temperatures are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

deviation of the two runs from the mean at the maximum pressure was 0.5%, at 75° 4.4%, at 125° 0.7%, and at 175° 0.3%. The adjustments necessary to secure agreement between the compressions and the freezing parameters were unimportant except at 175°, where a maximum adjustment of $- .0029$ was applied.

The freezing parameters are shown in Table XVI and Figure 6, and the compressions in Table XVII.

Carbon Bisulfide. The material I owe to Professor F. G. Keyes of M. I. T. who had prepared it as one of his standard liquids for fixed points for low temperature thermometry.

TABLE XVII

CHLOROFORM

 ΔV , cm³ per 1.489 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000	.000	.000	.000
6,200	.016) .077)*			
10,000	.104	.067) .119)*	.073	.079
14,000			.109) .155)*	
15,000	.130	.148	.161	.124
18,400				.148) .189)*
20,000	.150	.169	.185	.196
25,000	.167	.187	.203	.216
30,000	.181	.201	.218	.232
35,000	.194	.212	.230	.246
40,000	.204	.222	.241	.257
45,000	.213	.230	.250	.267
50,000	.221	.238		

* Solid at higher pressure.

The compressions were measured at all four temperatures with two set-ups at each temperature and in four pressure vessels. The freezing parameters were measured at 25° intervals from 25° to 175° with four set-ups, all in the same pressure vessel.

To secure agreement with previous results¹⁶ between 5,000 and 10,000 additive corrections of 0.0036 and - 0.0077 were applied at 25° and 75° respectively; these corrections are somewhat larger than usual. To secure agreement between measurements of compression and the freezing parameters, a maximum adjustment of 0.0017 was made at 25°, of 0.0000 at 75°, of .0010 at 125°, and of .0014 at 175°. The deviations at the maximum pressure of the two independent runs from the mean were 1.4% at 25°, 0.3% at 75°, 1.7% at 125°, and 2.3% at 175°.

The freezing parameters are shown in Table XVIII and Figure 7, and the compressions in Table XIX.

TABLE XVIII

CARBON BISULFIDE

Freezing Parameters

Pressure kg/cm ²	Temp. °C	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
0	-111°.6						
5,000	- 51.						
10,000	0	.0095	.0285	820	290	540	3.00
15,000	+ 46.	.0088	.0247	900	370	530	2.80
20,000	89.	.0084	.0222	960	440	510	2.64
25,000	130.	.0080	.0205	1,030	510	520	2.56
30,000	170.	.0078	.0195	1,110	590	520	2.50
35,000	209.	.0076	.0187	1,190	650	530	2.46

In addition to the normal reversible freezing investigated above, carbon bisulfide has near the extreme edge of the attainable range a highly unusual irreversible change. This has already been described,¹⁷ but for completeness will be mentioned again here. At temperatures of 175° or over and at pressures above 45,000, carbon bisulfide is transformed slowly and irreversibly into a black solid, permanent under atmospheric conditions, and by all the obvious tests a new form of CS₂. The density is about 4% greater than that of a mechanical mixture of the constituent elements. It has been suggested that it is a compound analogous to SiO₂; the structure, however, is too fine to check this suggestion by X-ray analysis.

Benzene, C₆H₆. The material was old stock from Timmermans,¹¹ kept sealed in glass.

Compressions were measured at 25° and 75° with two set-ups at each temperature and with two pressure vessels. At these temperatures the freezing pressures are so low as to be quite outside the range of this work, so that the compression measurements are on the solid phase. There is a previously known¹⁸ transition line running nearly vertically at approximately 12,500; the compression measurements therefore embrace the transition and for the most part are concerned with the high pressure modification of the solid.

There are no previous measurements of compression for comparison, and no correction was attempted at low pressures. The results are given in Table XX. The initial compression between 5,000 and 10,000 at 75° seems improbably higher than that at 25°, and probably all the results tabulated at 75° should be adjusted by an

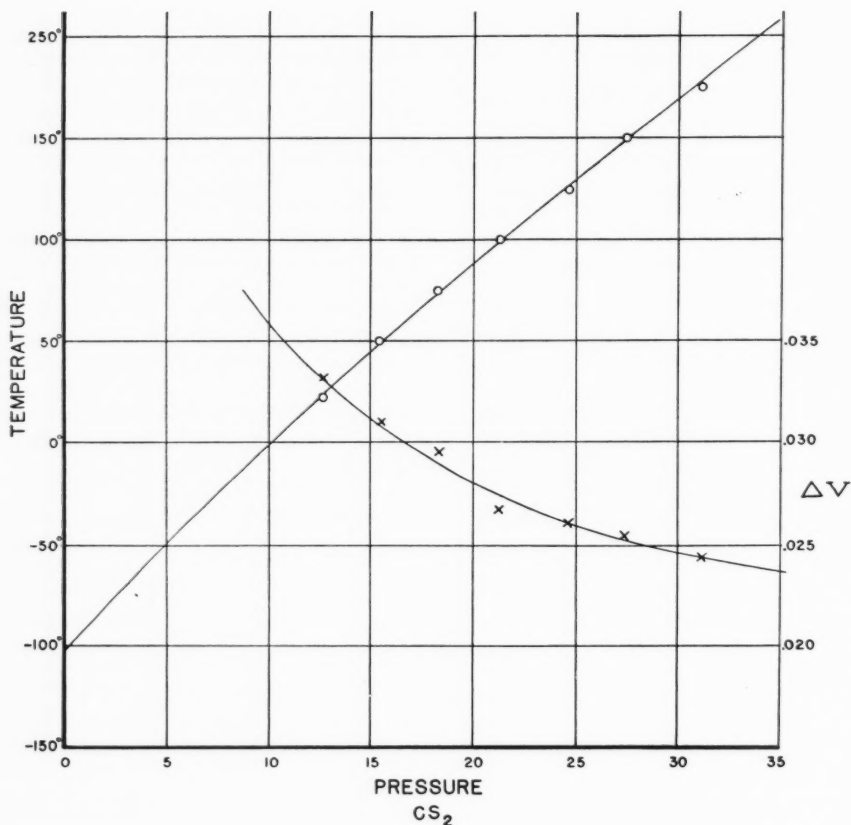


FIG. 7. The freezing parameters of carbon disulfide. The freezing temperatures are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

additive constant of perhaps -0.009 . The volume change at the transition has been previously determined to be $0.0090 \text{ cm}^3/\text{gm}$, against 0.0061 given by the unadjusted measurements. Since this transition occurs at the lower pressure end of the range the previous value is doubtless to be preferred. A correction was therefore applied to bring agreement; this correction is a maximum of 0.0025 at $12,500$ tapering off linearly to zero at $50,000$. The two runs differed from the mean at the maximum pressure by 3.0% at 25° and 3.9% at 75° .

Chlorobenzene. The material I owe to Professor F. G. Keyes, being one of his standard liquids. Compressions were measured at all four temperatures with two set-ups at each temperature and in four pressure vessels. Freezing determinations were made at 25° intervals up to 200° , with six

different set-ups in three different pressure vessels, giving, counting repetitions at the same temperature, fifteen determinations of the parameters. The large number of measurements of freezing was made necessary by the complexity of the phenomena. Chlorobenzene has a second modification of the solid, which replaces the ordinary form as the absolutely stable form at the higher temperatures. At the lower temperatures there is a strong tendency for the liquid not to freeze to the ordinary solid on passing beyond the normal melting line, but to freeze instead to the new form when the unstable prolongation of the melting line of the new form is reached. The solid thus formed by preference from the liquid is unstable with respect to the normal form, and it is a matter of caprice when and if at all it will flop irreversibly to the ordinary stable form. The

TABLE XIX

CARBON BISULFIDE

 ΔV , cm³ per 1.261 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000 (.827)	.000 (.845)	.000	.000
10,000	.063	.068	.073	.078
12,600	.086)*			
	.119)			
15,000	.132	.110	.118	.126
18,300		.131)*		
		.160)		
20,000	.155		.148	.159
24,400			.170)*	
			.196)	
25,000	.174	.187	.195	.184
30,000	.190	.204	.218	.204
30,700				.206)*
				.231)
35,000	.204	.217	.231	.243
40,000	.215	.229	.242	.255
45,000	.225	.239	.250	.265
50,000	.233	.248		

* Solid at higher pressures.

TABLE XX

BENZENE

 ΔV , cm³ per 0.878 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25°	75°
5,000	.000	.000
10,000	.036	.046
12,500	.049)*	.061)*
	.057)	.067)
15,000	.068	.079
20,000	.088	.099
25,000	.105	.116
30,000	.119	.131
35,000	.131	.143
40,000	.141	.153
45,000	.150	.162
50,000	.158	.170

* Solid II below this, solid I above.

appearances and floppings of the unstable form were unpredictable, and increased the difficulty of getting complete or even understandable data. The new form might appear in its region of instability at temperatures as low as 25°. At 75° and above the preference for the new form was so great that no points on the melting curve of the ordinary modification could be obtained in spite of the fact that thermodynamically it is the stable form, so that no good evidence could be obtained as to the exact location of the reversible triple point between two solids and liquid or of the transition line between the two solids.

There are previous measurements¹⁹ by which the low pressure compressions may be corrected only at 75°, the freezing pressure being too low at 25°. An additive correction of 0.0079 was applied at 75°. At 25° the two runs differed from the mean by 1.0% at the maximum pressure, at 75° by 2.3%, at 125° by 2.8%, and at 175° by 2.4%. At 75° the maximum adjustment necessary to make the compression results consistent with those for freezing parameters was 0.0053, at 125° 0.0002, and at 175° 0.0030. At 25° no adjustment was attempted of the compression of the solid at 10,000. At 25° the equilibrium pressure is 5,000; the compression listed for the solid at this pressure is merely the change of volume on melting as given by the freezing determinations. It is probable that the compression of the solid given in the table at 25° between 5,000 and 10,000 (0.034 = 0.079 - 0.045) is too high.

The freezing parameters are given in Table XXI and Figure 8 and the compressions in Table XXII.

Methylene Chloride. The material was prepared by distillation by Mr. L. D. Berger.

Compressions were measured at all four tem-

TABLE XXI

CHLOROBENZENE

Freezing Parameters

Pressure kg/cm ²	Temp. °C	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
Liquid—I							
0	- 45° .2						
5,000	+ 25.	.0164	.0402	730	200	530	2.47
10,000	80	.0124					
Liquid—II							
10,000	30	.0159	.0388	740	390	350	2.44
15,000	103	.0134	.0331	930	500	430	2.47
20,000	166	.0118	.0296	1,100	590	510	2.51
25,000	222	.0107	.0280	1,290	700	590	2.61

TABLE XXII

CHLOROBENZENE

 ΔV , cm³ per 1.107 gm. from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000	.000 (.883)	.000	.000
	.045			
10,000	.079	.058	.065	.071
13,000		.083		
15,000	.103	.122	.106	.111
16,700		.133	.117	
20,000	.123	.156	.152	.140
20,800			.167	.144
25,000	.140	.172	.183	.176
30,000	.154	.186	.197	.191
35,000	.166	.198	.208	.205
40,000	.177	.208	.218	.217
45,000	.186	.216	.226	.228
50,000	.194	.223		.237

* Solid I at higher pressures.

† Solid II at higher pressures.

peratures, with two different set-ups at each temperature and in five different pressure vessels. The freezing parameters were measured at 25° intervals from 25° to 150° with four different set-ups in three pressure vessels.

There are no previous measurements by which to correct the low pressure compressions.

At 25° the two independent compressions differed from the mean at the maximum pressure by 1.3%, at 75° by 3.4%, at 125° by 0.4%, and at 175° by 0.04%. An additional adjustment to bring the compressions into agreement with the melting parameters of 0.0031 at the maximum was applied at 25°, of 0.0011 at 75°, of .0030 at 125°, and of .0032 at 175°.

The melting parameters are given in Table XXIII and Figure 9 and the compressions in Table XXIV.

Ethylene Bromide. The material was from Timmermans.¹¹

The compressions were measured at 25° and 75°

TABLE XXIII
METHYLENE CHLORIDE
Freezing Parameters

Pressure kg/cm ²	Temp. °C	Slope $d\tau/dp$	ΔV cm ³ /gm	Lat. Ht. kg cm/gm	$p\Delta V$ kg cm/gm	ΔE kg cm/gm	ΔS kg cm/gm°
0	- 96°.7						
5,000	- 46						
10,000	0	.0088	.0338	1.050	340	710	3.86
15,000	+ 42	.0082	.0310	1.190	470	730	3.79
20,000	82	.0078	.0287	1.310	570	740	3.69
25,000	120	.0075	.0271	1.430	680	750	3.63
30,000	157	.0072	.0257	1.530	770	760	3.56

TABLE XXIV
METHYLENE CHLORIDE ΔV , cm³ per 1.336 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000	.000	.000	.000
10,000	.064	.069	.075	.081
13,000	.091			
	.134			
15,000	.144	.110	.116	.127
19,000		.134		
		.173		
20,000	.166	.176	.148	.159
25,000	.184	.198	.172	.185
25,700			.175	
			.211	
30,000	.198	.213	.228	.205
32,600				.214
				.247
35,000	.210	.224	.239	.253
40,000	.219	.233	.248	.263
45,000	.228	.240	.256	.272
50,000	.235	.246		

* Solid at higher pressures.

TABLE XXV
ETHYLENE BROMIDE ΔV , cm³ per 2.182 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25°	75°
5,000	.000	.000
10,000	.040	.045
15,000	.068	.075
20,000	.090	.097
25,000	.108	.114
30,000	.122	.129
35,000	.135	.142
40,000	.145	.152
45,000	.155	.162
50,000	.163	.171

with two different set-ups at each temperature and in two pressure vessels.

There are no previous values for check at low pressures. The deviation of the independent runs from the mean at the maximum pressure was 0.2% at 25° and 1.8% at 75°.

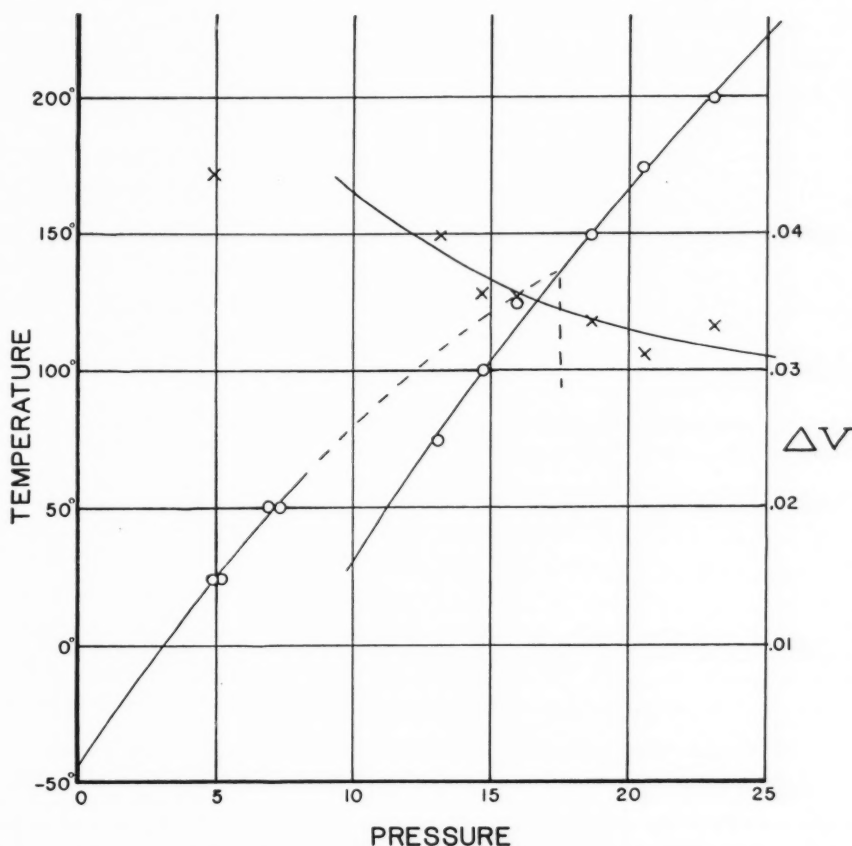


FIG. 8. The freezing parameters of chlorobenzene. The freezing temperatures are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right. The location of the triple point and the transition line between the two varieties of the solid is highly hypothetical.

The compressions are given in Table XXV. The normal freezing point is 10°, so that these measurements are all on the solid phase.

Cyclohexane. The source of the material was Timmermans.¹¹

Compressions were measured at all four temperatures with two different set-ups at each temperature and in four different pressure vessels. This material freezes at low pressures and rough values of the freezing parameters were determined incidentally in the course of the compression measurements. These freezing parameters are rough both because the special procedure for obtaining freezing parameters was not followed, and because the pressures were too low. In view of this, no effort was made to follow the freezing curve to higher temperatures.

At 25° the two compressions at the maximum pressure differ from the mean by 1.4% and at 75° by 0.02%, at 125° by 2.1%, and at 175° by 0.8%. There are no previous values for comparison. The compressions at the lowest pressures are more irregular than usual, and the adjustments are to a certain extent arbitrary.

The compressions are given in Table XXVI. The sequence of the values for change of volume on freezing is doubtless not as good as it would have been if direct determinations had been made of the melting parameters.

Methyl Cyclohexane. The material was old stock from Timmermans.

Compressions were measured at 25° and 75°. At each temperature four runs were made with four set-ups and two pressure vessels. Freezing

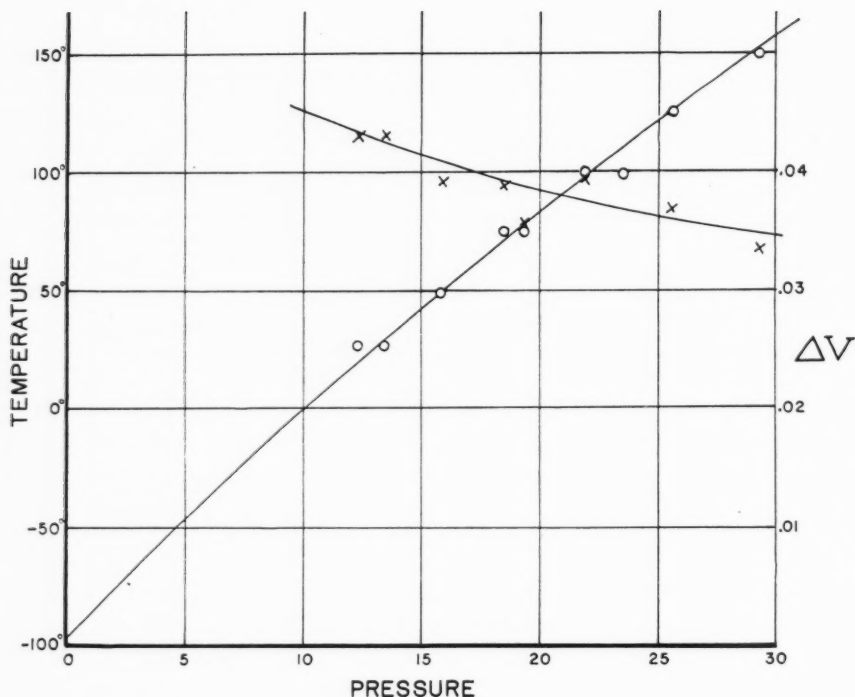


Fig. 9. The freezing parameters of methylene chloride. The freezing temperatures are shown by the circles, with the scale to the left, and the fractional changes of volume by the crosses, with the scale to the right.

occurs at comparatively low pressure, but freezing is very sluggish and if the normal time schedule is adhered to some of the subcooled liquid is carried up to the maximum pressure in spite of the fact that it is in contact with the solid. One half the runs were of this character. A rough estimate of the amount of liquid so carried in the unstable state to the maximum pressure can be obtained from the volume discontinuity at the melting point on release of pressure. To get the compressions of the pure solid phase, the regular time schedule had to be given up, delaying in the neighborhood of the freezing pressure until freezing was complete.

There are no previous values at the low pressures for comparison; on the other hand, at pressures below the melting point the compressions are now the average of four determinations instead of two as usual, and therefore should be more accurate. At 25° the deviation from the mean of the two runs on pure solid at the maximum pressure was 0.8% and at 75° 0.9%.

The compressions are given without attempt

at correction in Table XXVII. It is not probable that the abnormal sequence of volume discontinuity on freezing between 25° and 75° is correct. From the measurements on the partially frozen liquid the following rough statements can be made; at 25° the compression between 20,000 and 50,000 of the subcooled liquid is 0.017 greater than that of the solid; at 75° the corresponding excess between 25,000 and 50,000 is 0.007. The first of these two values is to be given greater weight, being the average of two determinations differing from the mean by 10%, whereas the latter rests on only a single measurement under more unfavorable conditions because the quantity of liquid remaining unfrozen was only one half as great.

p-Xylene. The material was from Timmermans.

Compressions were measured at 25° and 75°, with two different set-ups at each temperature and in two different pressure vessels. Freezing occurs at pressures below 5,000, so that the measurements are for the solid phase. At 25° the

TABLE XXVI

CYCLOHEXANE

 ΔV , cm³ per 0.779 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000	.000	.000	.000
7,500	.028 .069*			
8,700		.043 .078*		
10,000	.084	.088	.055	.064
11,270			.066 .100*	
14,180				.098 .131
15,000	.110	.119	.125	.136
20,000	.130	.141	.150	.164
25,000	.146	.158	.169	.184
30,000	.160	.173	.183	.199
35,000	.171	.185	.195	.210
40,000	.181	.195	.205	.220
45,000	.190	.204	.212	.227
50,000	.198	.212		

* Solid at higher pressures.

two compressions differed from the mean at the maximum by 1.7%, and at 75° by 3.1%. There are no previous values of compression for comparison or correction.

The compressions are given in Table XXVIII.

Water. The material was distilled water from the laboratory tin still, freed from air by boiling in vacuum.

The freezing parameters have already been determined²⁰ up to 190°. The particular object of the present measurements was to get compressions of both liquid and solid phases over as wide a range as possible. The compressions were

TABLE XXVII

METHYL CYCLOHEXANE

 ΔV , cm³ per 0.764 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25*	75°
5,000	.000	.000
10,000	.056	.062
13,800	.086 .113*	
15,000	.118	.099
18,800		.120 .149*
20,000	.137	.153
25,000	.152	.169
30,000	.166	.183
35,000	.177	.195
40,000	.187	.206
45,000	.195	.215
50,000	.203	.223

* Solid below this.

TABLE XXVIII

p-XYLENE

 ΔV , cm³ per 0.861 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV	
	25°	75°
5,000	.000	.000
10,000	.029	.035
15,000	.051	.057
20,000	.069	.074
25,000	.083	.088
30,000	.095	.100
35,000	.105	.111
40,000	.113	.120
45,000	.121	.129
50,000	.128	.137

measured at the four temperatures, with two set-ups at each temperature and with four pressure vessels.

In order to secure agreement with the previously measured volume decrements between 5,000 and 10,000, an additive correction of -0.0013 was applied at 25° and of -0.0038 at 75°. At the two higher temperatures there are no previous direct measurements for comparison, but extrapolation gave an additive correction of -0.0022 at 125° and -0.0024 at 175°. In addition, corrections had to be applied to bring about reconciliation with the previous volume

TABLE XXIX

WATER

 ΔV , cm³ per 1.000 gm, from 5,000 kg/cm² as zero

Pressure kg/cm ²	ΔV			
	25°	75°	125°	175°
5,000	.000 (.873)	.000 (.893)	.000	.000
9,800	.057 .127*			
10,000	.128	.063	.066	.070
15,000	.147	.105	.112	.120
20,000	.162	.136	.146	.157
21,430		.144 .236†		
22,270	.169 .226†			
25,000	.234	.247	.173	.185
28,140			.186 .267‡	
30,000	.247	.260	.272	.207
35,000	.256	.270	.284	.226
36,560				.231 .302‡
40,000	.266	.278	.294	.310
45,000	.274	.286	.302	.317
50,000	.281	.293		

* Transition from liquid to Ice VI.

† Transition from Ice VI to Ice VII.

‡ Transition from liquid to Ice VII.

discontinuities at the phase changes. At 25° the maximum such adjustment was 0.004, at 75° 0.004, at 125° 0.006, and at 175° 0.003.

The compressions are shown in Table XXIX.

DISCUSSION.

The Melting Curves. The most important question to be answered by these new data is whether in the extended pressure range the melting phenomena begin to show any new tendencies not manifested by the previously determined curves, which were confined, except for water, to a pressure range of 12,000 kg/cm². Of the imaginable new tendencies, the termination of the melting curve in a critical point between liquid and solid would be certainly the most important. The possible existence of such a critical point has been brought up again recently by certain new theories of the liquid state and of melting.³

The thermodynamic earmarks of a critical point are the simultaneous vanishing of the difference of various thermodynamic properties of the two phases, such as the volume discontinuity, latent heat, entropy difference, and difference of internal energy. All of these, when plotted against pressure or temperature along the melting line, should vanish or tend to vanish simultaneously at the same pressure and temperature. The most casual inspection of the tables of melting parameters shows that this is even less the case than in the previous range. The reader will find it profitable, I think, to plot from the tables of melting parameters the slope, that is $d\tau/dp$, the volume discontinuity, the latent heat, the difference of energy, and the difference of entropy, all against temperature along the melting curve. Of these quantities Δv always decreases with increasing absolute temperature, and with but one exception, ethyl bromide, the curve of Δv is always convex toward the temperature axis in such a way as to afford no expectation that the curve will ever cross the axis at any finite temperature. The curve for ethyl bromide is linear, and a linear extrapolation would give a vanishing Δv at 140°, beyond the range of the measurements. I think, however, that one is entitled to disregard this example, when it is considered that the experimental error was unusually great, the whole curve resting on only three points, at the last of which a superpressure of 17,000 kg/cm² was required to produce freezing, and that this is the only example of such behavior of Δv among the substances of this paper or the many previously examined in a

lower pressure range. The significance of this behavior of Δv , considered by itself and apart from the simultaneous behavior of the other parameters, is thus that there is no indication at present of the ultimate appearance of a critical point in the melting curve. No more is there any indication of a maximum, for a maximum means a vanishing of Δv at a finite temperature. Furthermore, if there were a maximum, the Δv curve would plunge vertically into the temperature axis, and the curvature is in the wrong direction for this.

The conclusions from an examination of the behavior of Δv alone are only reinforced when the simultaneous behavior of the latent heat, energy and entropy differences are considered. There is no tendency for any of these quantities to vanish at any finite temperature, to say nothing of any possible simultaneous vanishing with Δv . The curves for these three quantities in general rise, or if they fall, it is only by small amounts and irregularly. The superficial appearance of the graphs for these three quantities suggests a qualitative difference of behavior in this new high pressure range compared with the previous results to 12,000. Formerly, the latent heat had roughly a tendency to remain constant, or if it increased, the increase was in all cases less rapid than the increase in absolute temperature, so that in all cases the entropy difference between solid and liquid decreased with rising pressure and temperature along the melting curve. Now, in the new range, the general impression is that the latent heat tends to rise more rapidly with temperature, and in fact the rise is so rapid that now there are several cases of an increase of entropy difference along the melting curve. It may possibly be only fortuitous that these cases of increasing entropy difference appear to be associated with an increase in the pressure range, for it is to be considered that now several so-called abnormal substances have been taken within the scope of the measurements. There are only three substances which exhibit this increase of entropy difference to a marked degree, water (the parameters of which beyond 12,000 had been previously determined), ethyl alcohol, and n-butyl alcohol. The alcohols are known to be abnormal in certain respects, and water is certainly considered abnormal. Two other substances of this paper also show an increase of entropy difference, chlorobenzene and carbon bisulfide, but the increase is only slight. A rough characterization of the substances of this paper

in the new high pressure range is that with the exception of water and the two alcohols the entropy difference between solid and liquid tends to remain constant with rising pressure and temperature along the melting curve. There are obviously two factors affecting the entropy difference: it tends to increase because of increasing temperature, and tends to decrease because of the decrease of volume with increasing pressure. With the exceptions noted, these two tendencies roughly compensate each other. It will appear later that in general the effect of pressure on volume along the melting line is dominant over that of temperature, so that in general the volume of both liquid and solid phases decreases with increasing pressure along the curve, in spite of the effect of temperature in the opposite direction.

There is a characteristic difference between the jump in internal energy for the transition from solid to liquid compared with the transition from one solid to another. It has been found in previous work that at pressures above 12,000 there is an increasing tendency for the term $p\Delta v$ to become numerically greater than the latent heat, so that for almost all polymorphic transitions between solids at high pressures the phase stable at the higher pressure, that is, the phase with smaller volume, has a greater internal energy than the low pressure phase, in spite of the fact that passage from low pressure to high pressure phase may be accompanied by an emission of heat. With melting, on the other hand, although the term $p\Delta v$ increases with increasing pressure over the entire range for all substances, numerically it shows no indication that it will ever become large enough to neutralize the latent heat, so that the internal energy of the solid remains less than that of the liquid over the entire range. Except for the two alcohols and water, the difference of internal energy is very nearly constant over the entire pressure range, and is roughly of the order of one half the latent heat. Incidentally the fact that $p\Delta v$ rises over the entire pressure range indicates by extrapolation that Δv will not vanish at any finite pressure.

In spite of the fact that the two alcohols and water belong to the so-called abnormal liquids, I think in speculations on theories of the liquid and of melting considerable significance should be attached to the rapid rise of latent heat and entropy difference for them. In particular, water at high pressures is supposed to have lost the abnormalities which disturb it at ordinary pressures, so that at high pressures its structure should be among

the simplest of all liquids measured here, and its behavior accordingly more significant.

The behavior of $d\tau/dp$ is capable of giving some information about the general shape of the melting curve. When plotted against temperature, in all these cases, as also in all previous cases, curves are obtained which are convex toward the temperature axis in such a way as to give no justification for the expectation that they will cross the axis at any finite temperature. If there were a maximum, the curves would plunge vertically into the temperature axis, with concave curvature, and if there were a horizontal asymptote, the curves would cut the axis at a finite temperature.

The general conclusion from this new work in a pressure range three or four times the previous range (except for water) is therefore the same as the conclusion from the previous work, namely that the melting curves of all measured substances are alike in being inconsistent with the existence of either critical point, maximum temperature, or temperature asymptote, and furthermore, they all indicate positively that the curves continue to rise to indefinitely high pressures and temperatures, with continually decreasing slope $d\tau/dp$ and continually decreasing volume discontinuity between solid and liquid. This new work suggests that at increasingly higher pressures cases become more numerous in which the entropy difference between solid and liquid increases along the melting line; there is no experimental basis for the expectation that this entropy difference will ever vanish.

Compressions. Perhaps the most immediately striking thing about the compressions is the narrow numerical range of the total compressions between 5,000 and 50,000. For nearly all the substances of this paper these cluster in the range 0.20 to 0.25, whether or not freezing occurs in the range. Three substances, benzene, ethyl bromide and p-xylene, are lower, being in the range 0.15 to 0.20, but these substances are solid over the entire range of measurement. Curiously enough, in view of the fact that at low pressures water is much less compressible than the average organic liquid, water is the only substance with compressions greater than the norm, its compressions lying between 0.27 and 0.33. The unusually large total compressions of water are due to the unusually large volume changes which accompany the phase changes. Compressions of the magnitude mentioned means for all substances, including water, that at 50,000 the absolute volume is

surprisingly close to six tenths of the initial volume at atmospheric pressure.

A comparison of the compressions under more nearly comparable conditions would be obtained by comparing figures only for the solid phases. At room temperature, practically all the substances of this paper which freeze at all are solid at 25,000. In Table XXX are given the incre-

TABLE XXX

Volume decrements between 25,000 and 50,000 kg/cm²

Solids		Liquids	
Methyl Alcohol.....	.053	Methyl Alcohol.....	.054
Ethyl Alcohol.....	.057	n-Propyl Alcohol....	.067
n-Butyl Alcohol.....	.053	i-Propyl Alcohol....	.066
Ethyl Bromide.....	.059	n-Amyl Alcohol.....	.063
n-Propyl Bromide....	.045	n-Butyl Bromide....	.070
Ethyl Acetate.....	.054	Ethyl Acetate.....	.061
n-Amyl Oxide.....	.059		
Chloroform.....	.054		
Carbon Bisulfide....	.059		
Benzene.....	.055		
Chlorobenzene.....	.054		
Methylene Chloride..	.051		
Ethylene Bromide...	.055		
Cyclohexane.....	.052		
Methyl Cyclohexane..	.051		
p-Xylene.....	.045		
Water.....	.047		

ments of compression on passing from 25,000 to 50,000. The range of numerical values, considering the range of composition of these liquids, is surprisingly low, from 0.045 for p-xylene and 0.047 for water to 0.059 for carbon bisulfide. The substances which are liquid in the range above 25,000 have, with the single exception of methyl alcohol, compressions larger than those of the solids, but even for the liquids the extreme figure is only 0.070 for n-butyl bromide. If it is true that the major part of the compressions at these high pressures is afforded by the compression of the atoms themselves, then the atoms which enter into the composition of these substances must have approximately the same compressibility. It must be more or less fortuitous, however, that the particular elements of these substances have such similar compressibilities, because there are plenty of other elements with greatly differing compressibilities, as may be seen from a table of the compressions of 17 elements up to 100,000 kg/cm² just published.²¹

A corollary of the close similarity of the curves of compression against pressure of the various substances is the similarity of the curves of compressibility, or first differences of the tabulated compressions. The mean compressibility in the

range 5,000 to 10,000 averages about 0.000012, and in the range 45,000 to 50,000, 0.0000018. Variation from these figures of more than 10% is not common. Roughly, the compressibility ($-(\partial v/\partial p)_\tau$) varies inversely as the pressure, which means that volume as a function of pressure is approximated by the formula $v_0 - v = \text{const.} \log p/p_0$, taking p_0 in the neighborhood of 10,000. This is the same simple formula that I found a number of years ago²² approximately to reproduce the behavior of liquids in the range between 1,000 and 12,000. The formula evidently is not good for indefinite extrapolation, because it demands negative volumes at sufficiently high pressures. However, the pressure at which volume would become negative is of the order of 10⁷ kg/cm², far beyond the present experimental range.

The compressions of the liquid and the solid phases are not of different orders of magnitude; as an average the compression at the maximum pressure of the solids of this paper is 25% less than that of the liquids. There are no cases in which the compressibility increases at the reversible freezing point on passing from liquid to solid, and in most cases there is a distinct decrease. There are a few cases, however, of which methyl and ethyl alcohols are examples, in which any drop of compressibility at the freezing point is within experimental error. In even these cases however, there is an obvious drop in the second derivative of volume with respect to pressure, the compressibility of the solid dropping off with increasing pressure at a less rapid rate than that of the liquid. In those cases where measurements can be made on both solid and subcooled liquid over a wide pressure range, the compressibility of the liquid remains greater than that of the solid at the same pressure over the entire range, the volume of the liquid continually approaching that of the solid as pressure increases.

The compressions are considerably greater at the higher temperatures for all substances. In computing the results no cross smoothing with respect to temperature on the isobars was attempted, so that the spacing of the isotherms in the tables is not always regular, and may well be in error. On the whole the spacing of the isotherms is as smooth as one has a right to expect. A higher compression at higher temperatures means that thermal expansion decreases as pressure rises. The numerical value of the change in thermal expansion can be found only in those cases where there are absolute values of the

volume at 5,000 from previous work. Where the absolute values are known it will be found that there are very considerable decreases in thermal expansion; thus for methyl alcohol the thermal expansion at 50,000 is only one third or one quarter of what it is at 5,000. Isolated cases will be found in which apparently a negative thermal expansion is demanded at the highest pressure; this I think is not to be taken seriously but is to be ascribed to experimental error.

The accuracy of the measurements is not sufficient to permit any statement about the behavior of the derivative $(\partial^2 v / \partial \tau^2)_p$ at high pressure. Neither is the accuracy high enough to give any certain information about small scale irregularities such as were found in previous work.⁶ These abnormalities might consist in an increase of compressibility or of thermal expansion with increasing pressure. Such abnormalities were always local, confined to a comparatively narrow pressure range. These abnormalities appeared to be characteristic of the individual substances at high pressures, and were supposed to arise from the irregular shapes of the molecules. There is no reason to think that such abnormalities do not continue into the pressure range of the present work, and in fact a number of examples were found. The accuracy was not great enough, however, to give sufficiently reproducible values for any such irregularities and the best course seemed to be to smooth right across them. In view of the approximately equal compressions of the different kinds of atoms of which the substances of this paper are composed, one would perhaps expect that such abnormalities would tend to become less at these high pressures.

The answers to certain general questions with regard to the behavior of the individual pure phases along the melting line are suggested by the regularities presented by the compressions. The first question is: does the volume of the single phases, solid or liquid, increase or decrease along the melting line? There are obviously two opposing tendencies; because of the rising temperature the volume tends to increase and because of the rising pressure it tends to decrease. The analytic expression is:

$$\left. \frac{dr}{dp} \right|_{\text{melting}} = \left(\frac{\partial r}{\partial p} \right)_\tau + \left(\frac{\partial r}{\partial \tau} \right)_p \frac{d\tau}{dp}$$

The first term on the right is negative and decreases numerically along the line; the second term is positive and each of its factors decreases. It appears that in general the negative term is

greater than the positive term, and remains greater at high pressure, so that in general the expectation is that the volumes of the pure phases decrease along the melting line, the increasing pressure overbalancing the increasing temperature. The data of this paper permit evaluation of the exact numerical values in those cases where the volume at 5,000 has been determined. Thus for water the volumes of the liquid on the melting line at 75°, 125°, and 175° are 0.749, 0.728, and 0.700 respectively. The corresponding values for the solid are 0.657, 0.647, and 0.629. Or the volumes of liquid ethyl alcohol on the melting line at 25° and 75° are 0.691 and 0.662, and those of the solid 0.656 and 0.629.

Or we may ask whether the internal energy of the pure phases increases or decreases along the melting line. The analytical expression for this is:

$$\left. \frac{dE}{dp} \right|_{\text{melting}} = - \left[\tau \left(\frac{\partial r}{\partial \tau} \right)_p + p \left(\frac{\partial r}{\partial p} \right)_\tau \right] + \left[C_p - p \left(\frac{\partial r}{\partial \tau} \right)_p \right] \frac{d\tau}{dp}$$

The two terms in the first bracket on the right hand side are of opposite signs; initially the first of the two preponderates, and the sign of the whole is negative. But at higher pressures the term $p \left(\frac{\partial r}{\partial p} \right)_\tau$ tends to remain constant whereas

$\tau \left(\frac{\partial r}{\partial \tau} \right)_p$ decreases. Substitution of numerical values for methyl alcohol shows that at 50,000 the sign has reversed and become positive, having started at 10,000 as negative. The second cluster of terms on the right includes only one negative term. $\frac{d\tau}{dp}$ is positive and becoming less. C_p ,

judging from the known behavior in the low pressure range more accurately measured, at first decreases slightly with rising pressure, but then reverses and at higher pressures increases moderately. $p \left(\frac{\partial r}{\partial \tau} \right)_p$ increases numerically because of

the factor p in spite of the decrease of $\left(\frac{\partial r}{\partial \tau} \right)_p$, but numerically it is much less than C_p , and without doubt remains less, so that the second cluster of terms is always positive. On the whole therefore $\frac{dE}{dp}$ remains positive as pressure increases indefinitely along the melting curve, and the energy of the pure phases therefore increases.

Finally, it is to be considered what substances are brought to freeze by the application of pressure. If we accept at its face value our generalization about the universal character of the melting curve, temperature rising indefinitely with rising pressure, it would mean that any substance can be brought to freeze at any temperature by the application of sufficiently high pressure. The numerical values are such that it is a fair expectation that 50,000 should be high enough to bring this about at room temperature for substances ordinarily liquid, except perhaps for some of the permanent gases. Of the gases perhaps only hydrogen and helium are candidates when it is considered that the melting temperature of nitrogen is elevated 86° by only 6,000 kg/cm² and that of argon 109° by the same pressure.²³ In spite of this expectation four of the 21 substances examined here have not been brought to freeze; these are: n- and i-propyl alcohol, n-amyl alcohol, and n-butyl bromide. The factor which negates the expectation deduced from the universal behavior of the melting curve is evidently the enormous sluggishness of activity in the liquid at high pressures, which may have as a special result greatly increased subcooling before freezing will start, and after the nucleus of the solid has been formed, enormously retarded velocity of the reaction from liquid to solid. The case of methyl cyclohexane will be recalled in which liquid and solid phases were simultaneously present for more than one hour, during which barely one tenth of a total volume of less than 1 cm³ crystallized. The enormously increased viscosity of many liquids produced by pressure is evidently another aspect of the same phenomenon.²⁴

It would appear then that as a practical matter one may expect certain liquids will never be made to freeze by any pressure no matter how high. What a sufficient criterion might be of what these liquids are does not at present appear; it is curious that among the alcohols it is the alternate members of the series. Doubtless small amounts of impurity play an important part here. It is probable, furthermore, that liquids which cannot be made to freeze by any pressure will nevertheless be solids in the popular sense at high pressures, being in the glassy state, so that as far as certain classes of phenomena go, they might as well have frozen in the technical thermodynamic

sense. The applications to geophysics need not be elaborated.

In spite of the enormously increased sluggishness of many of these substances with respect to freezing, melting always occurred, as closely as could be told, immediately on crossing the thermodynamic melting line, so that the generalization remains that solids cannot be superheated with respect to the liquid. The only exception known is the case of certain complex silicates reported from the Geophysical Laboratory a number of years ago.

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